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Coal Fly Ash Trace Element Mobility in Soil Stabilization

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KEYWORDS: soil stabilization, fly ash

INTRODUCTION

Many coal combustion by-products (CCBs) have advantageous properties for engineering, construction, and manufacturing applications.^{1, 2, 3} CCBs have properties that are beneficial in soil stabilization applications such as soil drying, a soil amendment to enhance subgrade support capacities for pavements and floor slabs, reduction of shrink-swell properties of soils, and a stabilizer in aggregate road base construction and asphalt recycling. Approximately 31% of all U.S. CCBs (fly ash, bottom ash, boiler slag, and flue gas desulfurization materials) produced in 1999 were utilized. Six percent of the utilized fly ash and 20% of the utilized bottom ash was used in road base and subbase applications in 1999.⁴ The typical usage rate of CCBs for soil stabilization applications is 6%–15%, although this varies on the basis of engineering performance in prescribed laboratory tests.

Laboratory batch-leaching tests have been utilized to determine the potential impact of CCBs on the environment in numerous articles in the literature. The most common laboratory-leaching tests are 1) the toxicity characteristic leaching procedure (TCLP), U.S. Environmental Protection Agency (EPA) Method 1311;⁵ 2) the synthetic precipitation leaching procedure (SPLP), EPA Method 1312;⁶ and 3) the American Society for Testing and Materials (ASTM) D3987 leaching procedure.⁷ TCLP is generally not a suitable leaching test for the evaluation of field behavior of CCBs, as it was designed for the evaluation of leaching of wastes when codisposed in a sanitary landfill. SPLP and ASTM D3987 are more appropriate for evaluating the environmental performance of CCBs. The use of CCBs in various applications, including paving, embankments, and road base has resulted in little-to-negligible impact on ground and surface water quality.^{8, 9}

Although field-leaching behavior cannot be accurately duplicated with laboratory leaching, the mobility of constituents in materials to be placed in the environment can be estimated. The Minnesota Pollution Control Agency (MPCA) recommended the use of SPLP and a pH-neutral leaching test. The ASTM D3987 leaching procedure was chosen as the pH-neutral test, using distilled, deionized water for the leachate. These are short-term, 18-hour tests and do not allow adequate time for secondary mineralization to occur with the subsequent change in the materials controlling long-term behavior. The use of long-term leaching (LTL), typically 30- and 60-day

equilibration times at the Energy & Environmental Research Center (EERC), can demonstrate an increase or decrease in the mobility of the constituents of interest with respect to time. Under static laboratory batch-leaching conditions, these changes are dependent on chemical and mineralogical changes rather than on dilution or dispersion.

Secondary mineralization of CCBs has been shown to play an important role in the mobility of constituents from CCBs and CCBs combined with other materials.^{10, 11, 12} These reactions frequently take extended periods of time and may occur over days or even months. Ettringite, a mineral having the nominal composition $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, is an example of a secondary hydrated mineral. Ettringite is also the family name for a series of related compounds. Ettringite is a primary hydration product that forms when coal ash and water combine under alkaline conditions with a nominal pH between 11.5 and 12.5. The formation of ettringite and other secondary minerals can benefit the physical and engineering performance of stabilized soils. Ettringite formation acts to “dry” wet sites by incorporating large amounts of water into the CCB as it hydrates and improves handling properties of the soils as well as adds strength and reduces permeability. The secondary mineralization of field samples must occur prior to or during laboratory testing, so that laboratory results can best simulate real-world conditions. Ettringite is unique in that several elements that exist as oxyanions in aqueous solutions can substitute for the sulfate in the structure. These elements include but are not limited to arsenic, boron, chromium, molybdenum, selenium, and vanadium. Additionally, a decrease in the concentrations of major cations and anions such as calcium, aluminum, and sulfate often occurs. Ettringite is also responsible for strength development in products (such as concrete and controlled low-strength material) that contain CCBs. Ettringite has been shown to form in several types of CCBs, including fly ash generated from the combustion of subbituminous and lignite coal.^{10, 11} Many fly ashes meet the requirements for ettringite formation, which are soluble calcium, aluminum, sulfate, alkaline pH, and adequate water.

Leachate concentrations in this report are compared to national drinking water standards and leaching regulations. The maximum contaminant level (MCL) is the highest level of a contaminant that the EPA allows in drinking water. The MCL of lead is listed as a treatment technique (TT), which is a required process intended to reduce the level of contaminant in drinking water. It is then given an action level, which if exceeded in over 10% of the homes tested, triggers treatment. The secondary drinking water regulations (SDWR) are nonenforceable federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.¹³ Resource Conservation and Recovery Act (RCRA) and Universal Treatment Standards (UTS) leaching levels have been historically based on TCLP tests but can be used as a guideline when analyzing results from other leaching tests.

EXPERIMENTAL

Twelve sites were chosen to demonstrate the environmental and engineering performance of fly ash in soil stabilization in Minnesota. The sites consisted of various fly ash-stabilization projects. Two sites were subgrade stabilization prior to the

placement of a sand base and concrete inside buildings. There were two street subgrade sites with fly ash-stabilization prior to the placement of a base course and wear surface. A 2-mile stretch of road subgrade was performed with each one-half mile stabilized with different fly ashes, making four sites. Two sites were subgrade stabilization beneath parking lots prior to the placement of a base course and wear surface. Another site was a water main trench backfill, where the soil and fly ash were mixed, backfilled into the trench, and compacted. The remaining site was a simulated rainfall demonstration comparing/contrasting fly ash- and agricultural lime-stabilized plots. Only the leachates of the fly ash-stabilized plots will be discussed. The addition rate of fly ash was 12 or 14 parts added to 100 parts soil.

Stabilized soil samples were collected in core tubes. Duplicate fly ash-stabilized soil core tubes were received from several locations at each site. One core from each of the locations was disaggregated and used to make a composite for each site. The core tubes were stored sealed for at least 7 days. This allowed for strength development and accompanying mineralogical transformations to occur. A composite of the four fly ash-stabilized soil plots from the simulated rainfall demonstration was made in the laboratory.

Each stabilized composite was subjected to SPLP, ASTM D3987, and LTL tests. The ASTM D3987 and SPLP leachings had equilibration times of 18 hours. The SPLP extraction fluid was prepared by adding a 60/40 weight percent $\text{H}_2\text{SO}_4\text{--HNO}_3$ solution to distilled, deionized water until a pH of 5.00 ± 0.05 was reached, which is used to determine the leachability of soil for sites west of the Mississippi River. The ASTM D3987 and LTLs used distilled deionized water. The equilibration time for the LTL of the composites was 30- and 60-days. Four separate leachings were done for each sample. A 20:1 liquid-to-solid ratio with end-over-end rotation at 30 rpm was used for all leachings. The leachates were filtered through a $0.45\text{-}\mu\text{m}$ filter, and the pH of the filtered solution was recorded. The solutions were preserved with nitric acid to pH less than 2. The elements required for evaluation in MPCA Permit SW-532 were antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, iron, lead, manganese, mercury, molybdenum, nickel, selenium, silver, sulfate, thallium, vanadium, and zinc.

RESULTS AND DISCUSSION

The leaching values of the fly ash-stabilized soil composites varied between sites because of the differences in fly ash and bulk soil compositions, as well as because of potential geochemical changes induced through ash-sediment interactions and hydration reactions of the fly ash. The SPLP concentrations were, in many cases, higher than the 18-hour ASTM D3987 leachate concentrations although each was an 18-hour test. This is most likely due to the instantaneous effect of the acidic pH leaching solution.

Two sites used fly ash from plants that burn 5–10% petroleum coke. Therefore, higher leachate concentrations can be expected for Mo, Ni, V, and other trace elements that can be associated with petroleum coke in these two sites. Table 1 shows the range of

leachate values above the LLQs for all leaching tests performed. These values are compared to the MPCA LLQs and regulatory limits. All values are well below RCRA and UTS limits. One values for chromium is above the MCL. A few values are above the SDWR for sulfate. Few concentrations above MPCA required lower levels of quantitation (LLQs) were noted for Cd, Co, Fe, Pb, Mn, and Hg, and no concentrations above the required LLQs were seen for Sb, Be, Tl, or Zn in any of the leaching tests performed. Since a detection limit below the MCL for Be and Tl was achievable, the LLQ was lowered to 1 µg/L at the EERC, which showed actual Tl concentrations but no Be concentrations. A 30-day leaching of one site was not performed because of a lack of material.

Table 1

Comparison of Leachate Concentrations to MPCA LLQs and Regulatory Limits, µg/L

Element	LLQ	Range	Regulatory Limits	Element	LLQ	Range	Regulatory Limits
Sb	3		6 ^a ; 1500 ^e	Mn	5	8	50 ^c
As	4	4.4–14	50 ^a ; 5000 ^{d,e}	Hg	0.01	0.03–0.066	2 ^a ; 200 ^d ; 25 ^e
Ba	10	42–296	2000 ^a ; 10000 ^d ; 2100 ^e	Mo	2	2.5–285	
Be	1		4 ^a ; 1220 ^e	Ni	4	4.3–10	11000 ^e
B	200	250–1600		Se	2	2.1–7.1	50 ^a ; 1000 ^d ; 5700 ^e
Cd	0.3	0.96	5 ^a	Ag	0.3	0.34–5.3	100 ^c ; 5000 ^d ; 140 ^e
Cr	1	2.0–131	100 ^a ; 5000 ^d ; 600 ^e	Tl	1	1.01–1.38	2 ^a ; 20 ^e
Co	2	2.2–2.8		V	40	43–442	1600 ^e
Fe	10	11–42	300 ^c	Zn	30		5000 ^c ; 4300 ^e
Pb	2	9.2	15 ^{a,b} ; 5000 ^d ; 75 ^e	SO ₄ ²⁻	100 0	16,400– 640,000	250,000 ^c

^a MCL. ^b Treatment Technique. ^c SDWR. ^d RCRA. ^e UTS.

Indirect evidence of ettringite formation is seen in some of the composite samples. It is also known that ettringite is the primary secondary hydration product formed when alkaline coal ash reacts with water. If the proper ingredients: aluminum, calcium, sulfate and alkalinity are present, ettringite forms.¹⁴ Optimal pH levels for ettringite formation are 11.5 to 12.5. Although this optimal pH range is required for ettringite formation, the bulk pH of samples may be below this limit and ettringite can still form. This is because of localized high pH at the ash granule–water interface. Several trends of decreasing concentrations of trace elements can be seen in the elements arsenic, barium, boron, selenium, and sulfate. The decreasing concentration seen in barium is likely due to precipitation as barium sulfate where the others, which are oxyanions in aqueous

solution, may likely be due to ettringite formation as well as to various other less likely precipitation reactions.

The final pH levels of all the filtered fly ash-soil stabilized composite leachates are alkaline. The pH values for most of the samples were higher with distilled, deionized water and lower for an acidic leaching solution, as would be expected. Minor discrepancies between the two 18-hour tests, are likely due to slight nonhomogeneity of the samples and are also within experimental error for field samples of this type. The pH for 30- and 60-day leachings appears to increase with most of the fly ash-modified samples. Although the SPLP was an acidic leaching solution, the actual amount of acidity in a low ionic strength and unbuffered solution of this type is very low when compared to the available alkalinity of ash and buffering capacity of soil-ash systems. Differences in trace element concentrations and pH because of the use of an initially acidic solution, such as that used in SPLP leaching, may be due to an initial and near instantaneous effect of the acidic solution at the moment of first contact with sediment-ash systems. The general observation for these pH determinations is that all of the mixtures were potentially capable of ettringite formation. Direct evidence for ettringite formation can be obtained using x-ray diffraction but only at levels of greater than 1%. Because of the low loading of ash used in these projects, it would have been problematic to directly determine if ettringite had formed. The reduction of boron concentrations as well as decreases in concentrations of other oxyanionic element species with extended equilibration times in LTL, however, is fairly good indirect evidence for ettringite formation given the high solubility of most boron compounds and minerals and because of the resistance of boron to sorptive removal. Because ettringite formation can result in very efficient removal of select oxyanionic species (>99%), its formation in ash projects is highly desirable.¹⁵

CONCLUSIONS

There are several issues associated with the lower levels of quantitation specified in this research project. The LLQs specified are more than adequate for determination of potential adverse environmental impact within the framework of understanding of toxicity of inorganic trace elements. Mercury is a special issue, however, because of the extremely low potential detection limit offered by modern atomic fluorescence instrumentation. Mercury can be detected down to 0.1 absolute mass of mercury using atomic fluorescence detection. The problem in detection of mercury at this concentration level lies in reducing blank mercury levels in reagents and laboratory air to below what is necessary for determination of picogram levels. Mercury concentrations in rain can be as high as 10 ng/L posing some interesting questions regarding attempting to determine leachate concentrations to 0.2 ng/L which may not be an attainable concentration level considering the concentration of mercury in the source rain water. Additionally, mercury in mercury amalgam fillings in laboratory personnel can be problematic during sample preparation and analysis unless special precautions are taken to divert or treat exhaled air. It may not be possible to perform accurate mercury analyses at these detection limits for routine monitoring of potential mercury release under environmental conditions. It is likely that environmental monitoring under field

conditions could be extremely expensive and problematic. The LLQs specified for other trace elements, although low, are achievable using conventional techniques.

The concentrations obtained from leaching the core composites could have been interpreted more thoroughly if the soils and fly ashes had been leached individually. This would have provided more information as to how the addition of fly ash to the soils affected the mobility of elements.

It has been demonstrated in numerous research projects that alkaline coal fly ash reacts with water and forms hydration products that are considerably different from the original constituents of the ash. Hydration products, often referred to as secondary hydrated phases, contain the mineral ettringite as a primary hydration phase. Observations in the lab have led us to believe that ettringite always forms in alkaline ash hydration. During the formation of ettringite, several trace elements, including arsenic, boron, chromium, molybdenum, selenium, and vanadium, can be fixed into the crystalline structure of this mineral. Since the formation of ettringite and ash hydration in general can take from days to months, a leaching test with an 18-hour equilibration time such as that of the SPLP has too short a duration to accurately predict leaching. For this reason, the authors recommend a leaching test with a minimum of 30 days' equilibration time.

Overall, this study confirms the outcomes of other similar studies that fly ash, if used properly, is not a hazard to the environment when used for soil stabilization at the addition concentrations used in the sites for this project. Results of the runoff testing would lead one to the conclusion that stabilization with ash might be a recommended method.

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ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy National Energy Technology Laboratory under Cooperative Agreement No. DE-FC26-98FT40321 and by the Electric Power Research Institute (EPRI).). However, any opinions, finding, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE and EPRI, and no official endorsement should be inferred. Information about the Energy & Environmental Research Center can be found on its Web site at www.undeerc.org.